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Computer-Aided Prediction of ^{125}Te and ^{13}C NMR Chemical Shifts of Diorgano Tellurides

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Esse trabalho descreve um método para previsão dos deslocamentos químicos de RMN de ^{125}Te e ^{13}C de diorgano-teluretos baseado em uma abordagem tridimensional. Para tanto, 150 substâncias foram selecionadas da literatura e tiveram suas respectivas geometrias otimizadas através do método semi-empírico PM3. A partir desses dados, as estruturas foram codificadas através do programa FOCOS, que descreve o ambiente químico de cada átomo presente na estrutura, num total de 1411 focos para as substâncias. O método descrito foi testado com dez diorgano teluretos não inseridos na base de dados e mostrou uma exatidão maior na previsão de deslocamentos químicos de RMN de ^{125}Te e ^{13}C do que os dados previstos por um programa comercial. Os dados e os parâmetros estatísticos obtidos nesse estudo demonstram que o método aplicado foi capaz de prever com sucesso os deslocamentos químicos de RMN de ^{125}Te e ^{13}C dos diorgano teluretos.

This work describes a method to predict the ^{125}Te and ^{13}C NMR chemical shifts of diorgano tellurides based in a three-dimensional approach. For that, a collection of 150 compounds were selected from the literature and had their geometry optimized using the PM3 semi-empirical method. From this data, the structures were coded by the FOCOS program which described the chemical environment for each atom present in the structure, totalizing 1411 focos for the substances. The method developed was tested with ten diorgano tellurides not inserted in the database showing a higher accuracy in the prediction of ^{125}Te and ^{13}C NMR chemical shifts than those predicted by the commercial program. The chemical shifts and the statistical parameters obtained in this work demonstrate that the method applied was able to predict successfully the ^{13}C and ^{125}Te NMR chemical shifts of the diorgano tellurides.

Keywords: ^{125}Te NMR, ^{13}C NMR, chemical shift prediction, tellurides

Introduction

In the last decades, organic tellurium compounds have been applied as ligands in transition metal chemistry,[1,2] polymerization catalysts,[3,4] anti-oxidant agents[5-8] and synthetic intermediates.[9-12] In view of this interest in the organic compounds of this element, analytical methods for their rapid identification are welcome. Nuclear magnetic resonance (NMR) spectroscopy in nowadays is the routine technique of choice for this end. There are eight naturally occurring isotopes of tellurium. However, only ^{123}Te and ^{125}Te are active in NMR spectroscopy. The latter isotope is significantly more naturally abundant (7%) than the former one (1%). The ^{125}Te isotope is 12.5 times more receptive than ^{13}C.[13] In addition, ^{125}Te NMR presents a spectral width of about 7000 ppm.[14] Consequently, minor structural changes in a molecule cause sensitive chemical shift responses in its ^{125}Te NMR spectrum of compounds.

Considering the increasing importance of the organic tellurium compounds and the magnetic properties of ^{125}Te commented above, in this work we developed a method to predict the ^{125}Te and ^{13}C NMR chemical shifts of diorganotellurides based in a three-dimensional approach.

Theoretical approach

The structure determination of a new organic compound is currently made by coupling information derived from several spectroscopic methods with those obtained from 2D NMR spectroscopy. For this end, tables of chemical shifts,[15,16] are many times insufficient for the validation of complex and hypothetical structures. In order to help in the spectra analysis, a number of methods for ^{13}C and ^{1}H NMR chemical shift prediction have been developed. Basically, these

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methods use linear additive models, database retrieval approaches, empirical modeling or artificial neural networks techniques.[17-27] However, to the best of our knowledge, the methods up to now developed are unable to predict ^{125}Te chemical shifts. On the other hand, the ^{13}C NMR prediction for organotellurium compounds, by these methods are scarce and show large error ranges.

The three-dimensional database

A total of 150 diorgano tellurides were selected for this work. The ^{13}C and ^{125}Te NMR chemical shift data assigned in the literature were used. The structures of the selected compounds were optimized at the PM3 semiempirical level [28] employing the HyperChem program.[29] After the optimization process of the organo tellurides, their structures were coded by the FOCOS program,[30] which uses data derived from the optimized geometry and the reported ^{13}C and ^{125}Te NMR chemical shifts.

Atom codification

The following codes were computed for each carbon and tellurium atom using the geometrical and connectivity information obtained:

At_i-atom type code, that encodes the nature of the atom *i*, its hybridization state and hydrogenation pattern. Thirty three atom types (Table 1) were considered in the codification of the FOCOS program.

Sc_i-stereochemical code of tertiary and quaternary carbon atoms. For the chiral centers the codes 01 and 02 were attributed if the atom presents the *R* or the *S* configuration, respectively. For the achiral centers it was assigned the code 00.

The chemical environments were coded for the structure (all atoms) and designated as *foco*. The *foco* contains the atom type description (At_i) according to Table 1 for each element present in the structure, its respective stereochemical code (Sc_i) and all the neighboring atoms coded according to Table 1 and correlated with their distance from the centralized atom. The neighboring atoms are organized according to the increasing distance value from the focused atom. The maximum distance for the codification process can be selected by the user; in this study, the *focos* were constructed with the maximum distance of 5 Å. For each codified *foco*, the chemical shift value was stored together with the chemical environment.

All atoms *i* having the same *foco* were grouped into a cluster. Two *focos* atoms were considered as being equal if the distance tolerance is not larger than 0.25 Å. At the end of the clustering process, the mean chemical shift of the atoms belonging to the cluster was stored. The database elaborated contains 1411 *focos* for the 150 diorgano tellurides.

Results and Discussion

In order to predict the chemical shifts of the tellurium and carbon atoms, the three-dimensional model of the hypothetical structure was first constructed following the same method used for the database elaboration. Then the parameters of each atom of the structure were generated using the same variables as described above. To test the performance of the FOCOS program, ten diorgano

Table 1. Atomic groups and respective codes used in the molecular codification by the FOCOS program

Atomic groups	Code	Atomic groups	Code	Atomic groups	Code
$-CH_3$	01	=C=	12	– F	23
$-CH_2-$	02	=O	13	– Cl	24
$-\overset{\vert}{CH}-$	03	–OH	14	– Br	25
$-\underset{\vert}{\overset{\vert}{C}}-$	04	– O –	15	– I	26
$=CH_2$	05	$-NH_2$	16	– SH	27
=CH–	06	– NH –	17	– S –	28
$-\underset{\vert}{C}=$	07	$-\overset{\vert}{N}-$	18	=S	29
TCH–	08	=NH	19	$-\underset{\vert}{\overset{\vert}{S}}=$	30
TC –	09	=N –	20	$=\underset{\vert}{\overset{\vert}{S}}=$	31
HC*	10	TN	21	TP	32
C*	11	N*	22	Te (II)	33

T: triple bond representation; *aromatic atom representation.

tellurides not inserted in the database were selected randomly from the literature.[31-34] The structures of these compounds are shown in Figure 1.

The ^{125}Te and ^{13}C NMR chemical shifts predicted by the FOCOS program for these ten tellurides are shown in Table 2. The chemical formula were also submitted to the

Table 2. Experimental and predicted NMR chemical shifts (ppm)

	Compound **1**			Compound **2**			Compound **3**		
	Exp.	FOCOS	ACD	Exp.	FOCOS	ACD	Exp.	FOCOS	ACD
1	111.80	111.70	111.70	123.40	129.80	130.78	13.55	13.90	14.10
2	138.30	138.30	137.71	132.30	131.90	131.44	21.84	22.00	22.40
3	127.40	127.90	128.70	129.00	128.80	128.88	31.00	31.20	31.70
4	128.00	130.40	127.00	128.40	128.50	128.50	20.63	20.85	21.10
5	127.40	127.90	128.70	129.00	128.80	128.88	114.96	114.80	113.03
6	138.30	138.30	137.71	132.30	131.90	131.44	33.89	34.12	34.44
7	8.40	8.40	8.36	112.90	112.90	112.90	12.13	11.70	7.90
8	31.60	31.60	30.74	44.80	44.90	44.80	139.76	140.10	140.51
9	31.00	31.00	29.17	44.80	44.90	44.80	128.40	129.00	130.33
10	31.00	31.00	29.17	112.90	112.90	112.90	126.54	126.90	127.66
11	31.60	31.60	30.74	123.40	129.80	130.78	126.54	126.70	126.79
12	8.40	8.40	8.36	132.30	131.90	131.44	126.54	126.90	127.66
13	111.80	111.70	111.70	129.00	128.80	128.88	128.40	129.00	130.33
14	138.30	138.30	137.71	128.40	128.50	128.50	—	—	—
15	127.40	127.90	128.70	129.00	128.80	128.88	—	—	—
16	128.00	130.40	127.00	132.30	131.90	131.44	—	—	—
17	127.40	127.90	128.70	—	—	—	—	—	—
18	138.30	138.30	137.71	—	—	—	—	—	—
Te	468.00	394.60	—	361.00	332.00	—	456.00	448.00	—
Te	468.00	394.60	—	—	—	—	—	—	—

	Compound **4**			Compound **5**			Compound **6**		
	Exp.	FOCOS	ACD	Exp.	FOCOS	ACD	Exp.	FOCOS	ACD
1	140.50	141.40	140.55	13.85	13.90	14.10	13.33	13.90	14.10
2	130.10	128.70	129.66	22.31	22.00	22.40	21.66	22.00	22.40
3	131.50	131.30	130.22	31.71	31.20	31.70	30.98	31.20	31.70
4	119.50	119.00	121.33	20.99	20.85	21.10	20.49	20.85	21.10
5	131.50	131.30	130.22	112.60	113.10	111.26	114.29	114.80	111.71
6	130.10	128.70	129.66	33.74	33.25	33.49	32.57	32.95	32.59
7	4.80	6.30	4.14	6.27	5.98	3.87	16.45	18.10	29.62
8	4.00	3.20	2.62	43.48	41.50	39.68	25.28	25.10	24.78
9	34.10	34.10	34.63	53.08	54.95	56.94	25.28	25.10	24.78
10	25.20	25.20	25.20	26.12	26.00	25.87	—	—	—
11	13.40	13.50	13.40	—	—	—	—	—	—
Te	—	157.8	—	283.00	298.00	—	483.00	488.00	—

	Compound **7**			Compound **8**			Compound **9**		
	Exp.	FOCOS	ACD	Exp.	FOCOS	ACD	Exp.	FOCOS	ACD
1	110.90	110.45	109.93	-23.30	-22.40	-21.38	-22.70	-22.40	-21.66
2	143.80	143.10	141.13	5.20	6.75	15.24	-1.60	0.45	12.01
3	10.40	11.30	22.13	33.60	31.45	29.16	33.80	32.35	30.67
4	21.60	21.70	21.90	5.20	6.75	15.24	62.80	63.00	63.07
5	4.50	3.20	1.99	-23.30	-22.40	-21.38	—	—	—
6	34.00	34.10	34.25	—	—	—	—	—	—
7	25.20	25.20	25.20	—	—	—	—	—	—
8	13.40	13.50	13.40	—	—	—	—	—	—
Te	—*	—	—	104.00	107.50	—	105.00	107.50	—

	Compound **10**		
	Exp.	FOCOS	ACD
1	5.80	2.50	33.57
2	35.80	36.20	37.30
3	35.80	36.20	37.30
4	5.80	2.50	33.57
Te	234.00	245.00	—

*This data was not available in the original reference.

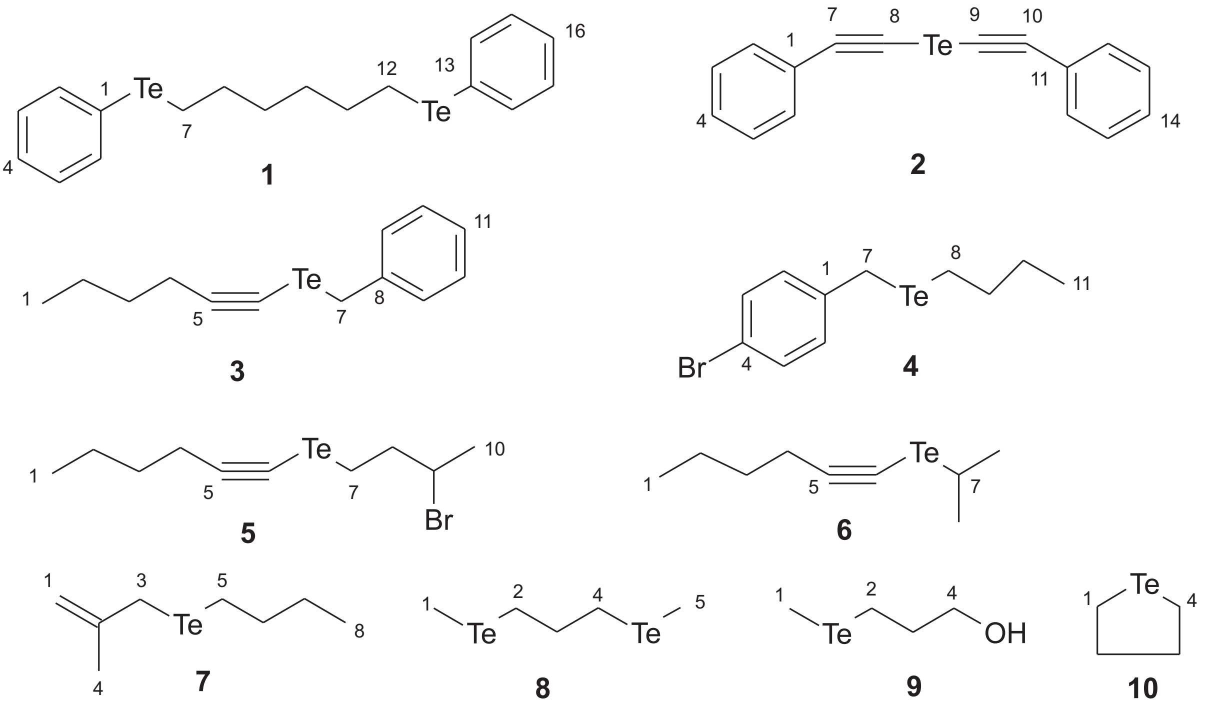

Figure 1. Tellurides used to test the programs.

commercial ACD program,[35] which predicted their ^{13}C NMR chemical shifts for the compounds (Table 2). For the compound **7** the ^{125}Te NMR data was not displayed in Table 2 because this data was not available in the original reference.

Analyzing the results generated by both programs one can observe that for ^{13}C NMR chemical shift prediction, the FOCOS program shows an average error of 0.67 ppm and a maximum error of 6.40 ppm, whereas the ACD program exhibits an average error of 2.11 ppm and a maximum error of 27.77 ppm. Linear regression of predicted against observed ^{13}C NMR chemical shifts for the FOCOS and ACD programs are displayed in Figures 2 and 3, respectively. The coefficients obtained from the regressions are displayed in the equations below. The main errors on the ^{13}C NMR chemical shift prediction were observed in both programs for the carbon atoms directly bonded to the tellurium atom (α-carbons), once these atoms show the typical high field resonance.

Equation for ^{13}C NMR data predicted from the FOCOS program:

Experimental = +0.99680(±0.00464) Focos +0.03896(±0.403839) (n=098; r=1.000; s=1.266; F=182507.818;)

Equation for ^{13}C NMR data predicted from the ACD program:

Experimental = +1.01349(±0.01845) ACD -2.06478(±1.608659) (n=098; r=0.996; s=4.936; F=11907.938;)

The data prediction carried out by the FOCOS program exhibits a higher accuracy than those predicted by the ACD program, because in the former the database was addressed for diorgano tellurides. This specific database shows atoms with similar chemical environments of the test compounds, resulting in smaller errors in the ^{13}C NMR chemical shift prediction. However, it was not possible to compare the ^{125}Te NMR data predicted by the FOCOS program with other commercial software because they do not present ^{125}Te NMR predictions.

Using the results obtained by the FOCOS program for the tellurium atom, a linear regression of the data predicted against the experimental chemical shifts was plotted (Figure 4). The coefficients obtained from the regression for the ^{125}Te data are shown in the equation below.

Equation for ^{125}Te NMR data predicted from the FOCOS program:

Experimental = +1.09859(±0.20254) Focos -14.52909(±68.598651) (n=009; r=0.978; s=34.224; F=156.452;)

The tellurium chemical shifts of diorgano tellurides are strongly dependent on the structure of the organyl

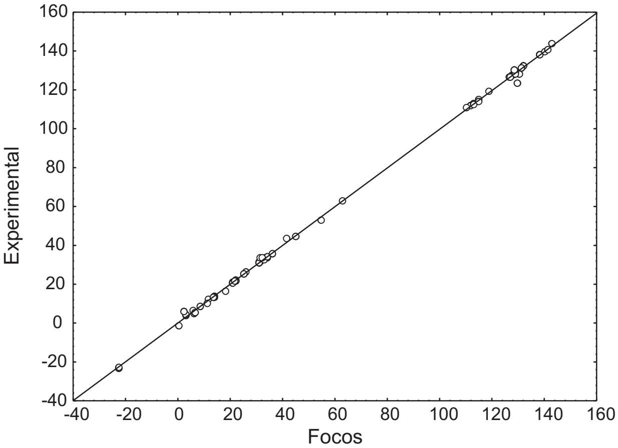

Figure 2. ^{13}C NMR chemical shifts (ppm) experimental *vs.* predicted by the FOCOS program.

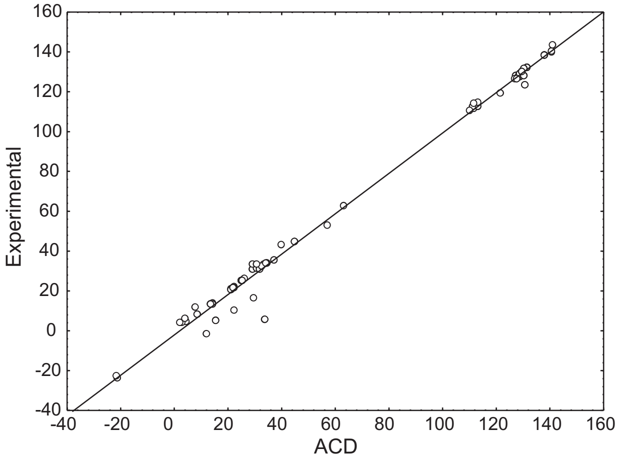

Figure 3. ^{13}C NMR chemical shifts (ppm) experimental *vs.* predicted by the ACD program.

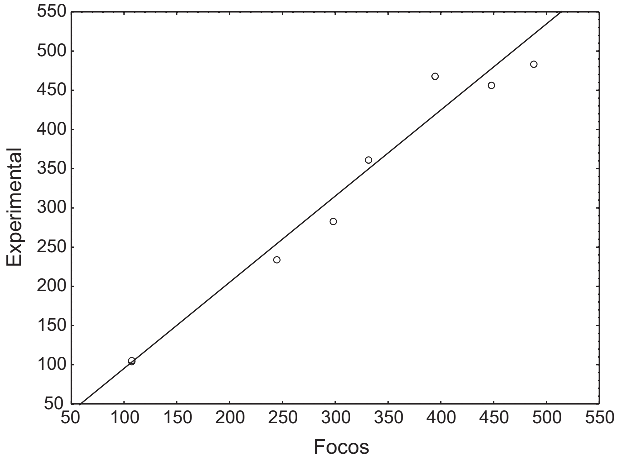

Figure 4. ^{125}Te NMR chemical shifts (ppm) experimental *vs.* predicted by the FOCOS program.

group. For compounds **1** and **2** the FOCOS program fails to reproduce adequately the experimental data. Note that these compounds have a Te substituent in a phenyl ring and in a phenyl –C≡C– conjugated system. Additionally, the ^{125}Te chemical shifts are dependent upon solvent, temperature and concentration of the sample. In this way, the prediction of ^{125}Te NMR chemical shifts is a hard task due to the number of variables involved. However, the data shown indicate that the values calculated by the methods described in this work agree satisfactorily with the experimental data.

The parameters obtained from the regression methods are statistically significant and demonstrate that despite of the experimental data show the large variation due to the higher sensibility to external factors, the method here described was able to predict successfully the ^{13}C and ^{125}Te NMR chemical shifts.

Conclusions

The method described in this paper allows the prediction of ^{125}Te and ^{13}C NMR chemical shifts of diorgano tellurides, employing a database that contains 150 substances. The three-dimensional code described is detailed enough to consider all atoms that can influence the magnetic behavior of the resonant atom. This approach lead to accurate results in the restricted structural domain of the diorgano tellurides, but could be extended to other heavy resonant atoms.

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